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CO₂ absorption in carbonate/bicarbonate solutions: The Danckwerts-criterion revisited

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Abstract

In industrial applications CO₂ is frequently removed from gas streams at elevated pressures by absorption and subsequent chemical reaction in carbonate/bicarbonate solutions (e.g. Benfield process). The criterion that determines whether or not this reaction can be regarded as pseudo-first order is given by Danckwerts and Sharma (1966), but its derivation has never been published. In the present study, a consistent set of equations and physico-chemical parameters is presented to describe the CO₂ absorption/reaction process. It was found that the criterion was justified, but should be somewhat confined to reduce possible errors. Furthermore, the model was validated by experiments in a stirred cell reactor up to CO₂ partial pressures of 16 bar.

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Keywords: Danckwerts-plot; CO₂ absorption; Mass transfer; Stirred cell; Elevated pressure

1. Introduction

The Danckwerts-plot technique (Danckwerts et al., 1963) is used in chemical engineering to simultaneously obtain the mass transfer parameters, k_L and a , from mass transfer experiments. From the measurements of the gas absorption rate, R_A (mole s⁻¹), at different apparent first order reaction rate constants the values of k_L and a can be determined simultaneously using the Danckwerts surface renewal model (Danckwerts, 1950) with a (pseudo) first order reaction:

$$\left(\frac{R_A}{m_{AC} V_L}\right)^2 = (k_L a)^2 + k_{1,app} D_A a^2. \quad (1)$$

When the left-hand side of Eq. (1) is plotted versus the apparent first order rate constant times the diffusion coefficient of the gas into the liquid ($k_{1,app} D_A$), the slope equals the squared specific gas liquid interfacial area (a^2) and the

intercept matches the square of the volumetric mass transfer coefficient ($k_L a$)². A commonly used reaction system for this method is a carbonate/bicarbonate buffer solution, in which the reaction between CO₂ and water can be catalyzed by a number of agents, e.g. hypochlorite and arsenite. The criterion that determines whether or not the reaction of CO₂ in a carbonate/bicarbonate buffer solution can be regarded as pseudo-first order is given by Danckwerts and Sharma (1966):

$$m_{CO_2} c_{CO_2(G)} \left(\frac{1}{c_{CO_3^{2-}}} + \frac{2}{c_{HCO_3^-}} \right) \times \left(\sqrt{1 + \frac{D_{CO_2} k_{1,app}}{k_L^2}} - 1 \right) \ll 1. \quad (2)$$

The reaction can be regarded as pseudo-first order when the concentrations of all the ions are uniform throughout the mass transfer zone. Although this Danckwerts-criterion is often referred to in literature, its derivation has never been published. Moreover, it was found that although the left-hand side of Eq. (2) is much smaller than 1, still large concentration gradients could exist, and thus considerable deviations

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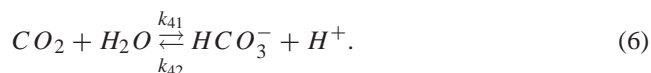
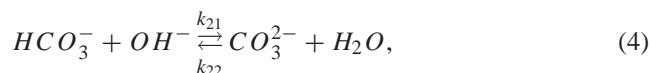
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from the pseudo-first order region may occur. The criterion is based on the fact that the transport of carbonate from the bulk can become the limiting step in the mass transfer process. However, due to the influence of both the carbonate and bicarbonate ions on the hydroxyl concentration in the mass transfer zone, a possible reduction in flux is difficult to predict on beforehand. Information regarding this criterion is therefore very important, both for research activities (the above-mentioned Danckwerts-plot technique), as well as for industrial purposes, in which CO_2 is frequently removed from gas streams at high pressure using chemical absorption in a liquid (e.g. the Benfield process, Benson et al., 1954). At these elevated CO_2 pressures the Danckwerts-criterion is violated more easily and accurate knowledge regarding the solution of the complete reaction system is therefore required.

To study the validity of the above criterion, the flux of CO_2 from the gas to the liquid phase was determined numerically by solving the mass balances for all components. Furthermore, the developed model was compared to mass transfer experiments up to a CO_2 partial pressure of 16 bar.

2. Reaction system

The following reactions occur in the carbonate/bicarbonate solution:



The corresponding equilibrium constants are defined as:

$$K_1 = \frac{c_{\text{H}^+} c_{\text{HCO}_3^-}}{c_{\text{CO}_2(\text{L})}}, \quad (7)$$

$$K_2 = \frac{c_{\text{CO}_3^{2-}}}{c_{\text{HCO}_3^-} c_{\text{OH}^-}}, \quad (8)$$

$$K_W = c_{\text{H}^+} c_{\text{OH}^-}. \quad (9)$$

The reaction rate per component is then given by:

$$r_{\text{CO}_2} = k_{12} c_{\text{HCO}_3^-} - k_{11} c_{\text{CO}_2(\text{L})} c_{\text{OH}^-} + k_{42} c_{\text{HCO}_3^-} c_{\text{H}^+} - k_{41} c_{\text{CO}_2(\text{L})}, \quad (10)$$

$$r_{\text{OH}^-} = k_{12} c_{\text{HCO}_3^-} - k_{11} c_{\text{CO}_2(\text{L})} c_{\text{OH}^-} + k_{22} c_{\text{CO}_3^{2-}} - k_{21} c_{\text{HCO}_3^-} c_{\text{OH}^-} + k_{32} - k_{31} c_{\text{OH}^-} c_{\text{H}^+}, \quad (11)$$

$$r_{\text{HCO}_3^-} = k_{11} c_{\text{CO}_2(\text{L})} c_{\text{OH}^-} - k_{12} c_{\text{HCO}_3^-} + k_{22} c_{\text{CO}_3^{2-}} - k_{21} c_{\text{HCO}_3^-} c_{\text{OH}^-} + k_{41} c_{\text{CO}_2(\text{L})} - k_{42} c_{\text{HCO}_3^-} c_{\text{H}^+}, \quad (12)$$

$$r_{\text{CO}_3^{2-}} = k_{21} c_{\text{HCO}_3^-} c_{\text{OH}^-} - k_{22} c_{\text{CO}_3^{2-}}, \quad (13)$$

$$r_{\text{H}^+} = k_{32} - k_{31} c_{\text{OH}^-} c_{\text{H}^+} + k_{41} c_{\text{CO}_2(\text{L})} - k_{42} c_{\text{HCO}_3^-} c_{\text{H}^+}. \quad (14)$$

The bulk concentrations of all species are calculated using the equilibrium constraints, the overall carbon balance and the electroneutrality constraint:

$$K_1 / K_W c_{\text{CO}_2(\text{L}),\text{bulk}} c_{\text{OH}^-,\text{bulk}} = c_{\text{HCO}_3^-,\text{bulk}}, \quad (15)$$

$$K_2 c_{\text{OH}^-,\text{bulk}} c_{\text{HCO}_3^-,\text{bulk}} = c_{\text{CO}_3^{2-},\text{bulk}}, \quad (16)$$

$$c_{\text{HCO}_3^-,\text{ini}} + c_{\text{CO}_3^{2-},\text{ini}} = c_{\text{CO}_2(\text{L}),\text{bulk}} + c_{\text{HCO}_3^-,\text{bulk}} + c_{\text{CO}_3^{2-},\text{bulk}}, \quad (17)$$

$$K_W - c_{\text{H}^+,\text{bulk}} c_{\text{OH}^-,\text{bulk}} = 0, \quad (18)$$

$$c_{\text{H}^+,\text{bulk}} + c_{\text{K}^+,\text{bulk}} = c_{\text{OH}^-,\text{bulk}} + c_{\text{HCO}_3^-,\text{bulk}} + 2c_{\text{CO}_3^{2-},\text{bulk}}. \quad (19)$$

The concentration profiles of all species in the mass transfer zone can be calculated as a function of time using the following equation:

$$\frac{\partial c_A(x, t)}{\partial t} = D_A \frac{\partial^2 c_A(x, t)}{\partial x^2} - z_A D_A \frac{F}{RT} \frac{\partial(\phi(x, t) c_A(x, t))}{\partial x} + r_A(x, t). \quad (20)$$

The electrostatic potential gradient (ϕ) can be calculated by the use of the Nernst–Einstein equation (Newman, 1973) assuming dynamic electroneutrality:

$$\phi(x, t) = \frac{RT}{F} \frac{\sum_{q=1}^{NC} z_q D_q \frac{\partial c_q(x, t)}{\partial x}}{\sum_{q=1}^{NC} z_q^2 D_q c_q(x, t)}. \quad (21)$$

The following boundary conditions are used:

$$t = 0, \quad x > 0 : c_A(x, t) = c_{A,\text{bulk}},$$

$$t > 0, \quad x = 0 : c_{\text{CO}_2}(x, t) = m_{\text{CO}_2} c_{\text{CO}_2(\text{G})},$$

$$t > 0, \quad x = 0:$$

$$D_{\text{ion}} \frac{\partial c_{\text{ion}}(x, t)}{\partial x} - z_{\text{ion}} D_{\text{ion}} \frac{F}{RT} \phi(x, t) c_{\text{ion}}(x, t) = 0,$$

$$t > 0, \quad x = \infty : c_A(x, t) = c_{A,\text{bulk}}. \quad (22)$$

The flux of CO_2 through the gas–liquid interface is calculated using the Higbie penetration model (Higbie, 1935). The complete system of equations was solved using the method of lines.

3. Physical parameters

The solubility and diffusivity of CO₂ in the 0.5 M/0.5 M potassium carbonate/potassium bicarbonate solution are given elsewhere (Cents et al., 2001). All physical parameters at 24 °C are given in Table 1.

The ionic diffusion coefficients have been estimated using the Nernst equation (Horvath, 1985):

$$D_A^\infty = \ell_A^\infty \frac{RT}{z_A F^2}. \quad (23)$$

The ionic conductivities at infinite dilution, ℓ_A^∞ , have been fitted to the experimental values of Horvath (1985).

4. Chemical parameters

The value of k_{11} in the presence of co-electrolytes is given by Pohorecki and Moniuk (1988):

$$\log \frac{k_{11}}{k_{11}^\infty} = 0.11 \times 10^{-3} c_{K^+} + 0.17 \times 10^{-3} c_{CO_3^{2-}}. \quad (24)$$

The influence of the bicarbonate ion was not given by these authors and was therefore neglected. The reaction rate constant at infinite dilution, k_{11}^∞ , is given by

$$\log k_{11}^\infty = 8.916 - \frac{2383}{T}. \quad (25)$$

Reaction 4 is fast as it involves only a proton transfer. The reaction rate constant, k_{21} , was determined to be $6 \times 10^6 \text{ m}^3/(\text{mol s})$ (Eigen, 1963). The neutralization rate constant, k_{31} , was also determined by this author and was $1.4 \times 10^8 \text{ m}^3/(\text{mol s})$. The reaction rate between CO₂ and water, k_{41} , is very slow (0.024 s^{-1} , Danckwerts and Sharma, 1966). This reaction can, however, be catalyzed by a number of agents. Cents et al. (2001) used sodium hypochlorite for which a reaction rate constant was determined to be $1.8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 294 K.

The backward reaction rate of reaction 3, k_{12} , is defined by the value of the equilibrium constant for this reaction ($k_{12} = k_{11} K_W / K_1$). K_1 is given as a function of temperature by Edwards et al. (1978):

$$K_1 = \exp \left(-\frac{12092.1}{T} - 36.786 \ln(T) + 235.482 \right) \rho_W, \quad (26)$$

where ρ_W is the density of water (kg/m^3).

The value of the solubility product K_W is taken from Tsonopoulos (1976):

$$\log \left(\frac{K_W}{\rho_W^2} \right) = -\frac{5839.5}{T} - 22.4773 \log(T) + 61.2062. \quad (27)$$

The equilibrium constant (K_2) at infinite dilution that determines the value of the backward reaction of reaction 4,

Table 1

Used physical and chemical parameters at 297 K for the absorption of CO₂ in a 0.5 M KHCO₃/0.5 M K₂CO₃ solution

Parameter	Value	Parameter	Value
k_{11} , $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.41×10^1	D_{CO_2} , $\text{m}^2 \text{ s}^{-1}$	1.59×10^{-9}
k_{12} , s^{-1}	3.11×10^{-4}	D_{OH^-} , $\text{m}^2 \text{ s}^{-1}$	5.17×10^{-9}
k_{21} , $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	6.00×10^6	$D_{HCO_3^-}$, $\text{m}^2 \text{ s}^{-1}$	1.18×10^{-9}
k_{22} , s^{-1}	1.22×10^6	$D_{CO_3^{2-}}$, $\text{m}^2 \text{ s}^{-1}$	9.20×10^{-10}
k_{31} , $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.40×10^8	D_{H^+} , $\text{m}^2 \text{ s}^{-1}$	9.21×10^{-9}
k_{32} , $\text{mol m}^{-3} \text{ s}^{-1}$	1.29×10^0	D_{K^+} , $\text{m}^2 \text{ s}^{-1}$	1.95×10^{-9}
k_{41} , s^{-1}	0.24×10^{-1}	m_{CO_2} , -	5.24×10^{-1}
k_{42} , $\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	5.71×10^1	ρ_W , kg m^{-3}	9.97×10^2

$k_{22} = k_{21}/K_2$, is given by Hikita et al. (1976):

$$\log(K_2) = \frac{1568.9}{T} - 2.5866 - 6.737 \times 10^{-3} T. \quad (28)$$

The values of the backward reactions, k_{32} and k_{42} can be calculated from the equilibrium constants and are k_{31}/K_W and k_{41}/K_1 , respectively.

5. Results

In Fig. 1 typical concentration profiles of the different components are presented. The absorption of CO₂ is enhanced due to the reaction, but this enhancement is less compared to the case when a pseudo-first order reaction is assumed, due to the depletion of hydroxyl ions near the interface. The average flux of CO₂ from the gas phase to the liquid phase is 23% lower, when the concentration profiles of all components are taken into account, compared to case with the assumption of a pseudo-first order reaction.

The significance of the Danckwerts criterion is shown in Fig. 2. The ratio of the actual flux and the flux when a pseudo-first order reaction is assumed is plotted versus the left-hand side of Eq. (2) for two different cases: by variation in the mass transfer coefficient k_L and by variation of the CO₂ partial pressure. In the variation of the k_L , a constant pressure of 1.0 bar was applied and in the variation of the pressure a constant k_L of $5 \times 10^{-5} \text{ m/s}$ was taken. The results show that the left-hand side of the equation should be less than 0.1 in order to sustain an error less than 3% when the assumption of a pseudo-first order reaction is made.

To test the modelling results, CO₂ absorption experiments were carried out at 24 °C in a 0.5 M KHCO₃/0.5 M K₂CO₃ buffer solution in a 640 ml stirred autoclave, which contained 300 ml of liquid. A stirring speed of 60 rpm was used, which ensured a flat gas–liquid interfacial area, as shown from experiments with different stirring speeds. In the experiments the CO₂ partial pressure was varied from 0.5 to 16 bar to change the value of the left-hand side in the Danckwerts criterion (Eq. (2)).

The mass transfer coefficient, k_L , of CO₂ in water was determined from the reactor pressure vs. time curve in which

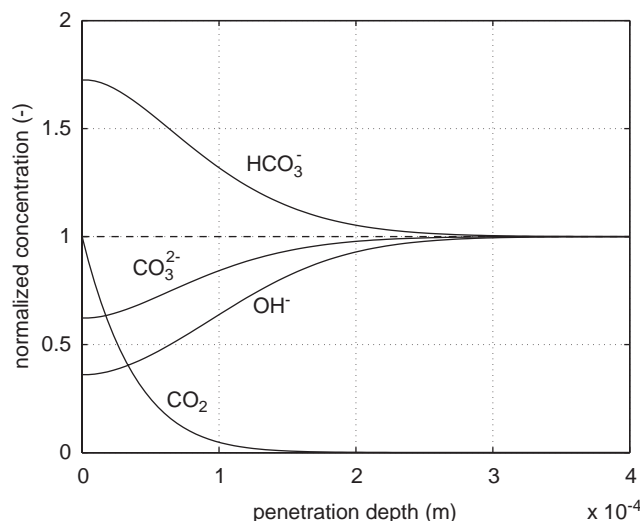


Fig. 1. Concentration profiles in the 0.5 M KHCO₃/0.5 M K₂CO₃ buffer solution at the end of the contact time. $p_{CO_2} = 4$ bar, $k_L = 2 \times 10^{-5}$ m/s.

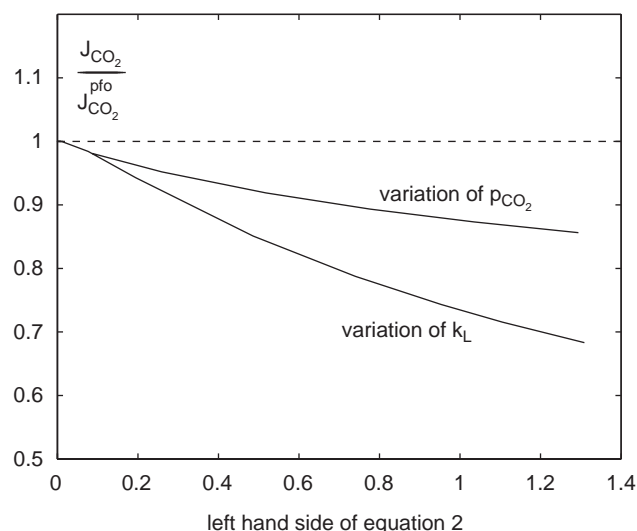


Fig. 2. Ratio of the flux calculated with the full model and the flux calculated with the assumption of a pseudo-first order (pfo) reaction.

the dissolved CO₂ concentration was taken into account. The value of the mass transfer coefficient in the buffer solution was estimated from experiments in pure water using a correction for the diffusion coefficient (the power of 0.6 was estimated from the work of Versteeg et al. (1987)):

$$k_{L, \text{buffer}} = k_{L, \text{water}} \left(\frac{D_{CO_2, \text{buffer}}}{D_{CO_2, \text{water}}} \right)^{0.6} \quad (29)$$

The value of k_L in pure water was not dependent on the pressure and was found to be 1.93×10^{-5} m/s. Application of Eq. (29) lead to an estimated k_L value of 1.75×10^{-5} m/s in the buffer solution. The flux of CO₂ in the buffer solution was determined from the pressure drop in a certain time

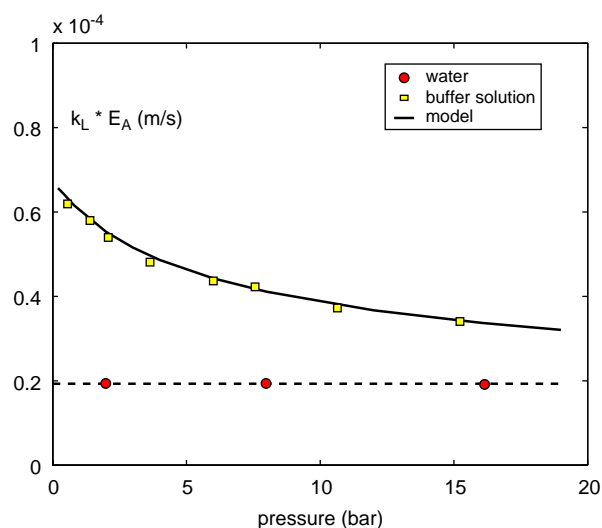


Fig. 3. $k_L E_A$ versus the pressure of CO₂ in a stirred cell reactor. Model line: 297 K.

interval. It was verified that the composition of the buffer did not change significantly during this time.

The results are presented in Fig. 3 and more details are given in Table 2. A reasonable agreement between the model and the experiments is obtained at low pressures (the model predicts a flux that is approximately 4% higher compared to the experiments). The effect of ionic strength on K_2 , which was taken into account by Roberts and Danckwerts (1962) and Hikita et al. (1976) (for sodium ions) was found to be too strong and caused an underestimation of the flux (via an underestimation of the OH[−] concentration) by almost a factor of 2 ($k_L E_A = 3.83 \times 10^5$ m/s) when making use of a correction for the presence of potassium ions:

$$\log \frac{K_2}{K_2^\infty} = \frac{1.01 \sqrt{c_{K^+}/1000}}{1 + 1.49 \sqrt{c_{K^+}/1000}} + 6.1 \times 10^{-5} c_{K^+} \quad (30)$$

Not taking this ionic effect on K_2 into account, was supported by two other measurements:

- Measurement of the CO₂ bulk concentration was performed by leading a small nitrogen stream through an intensely stirred buffer solution. It was verified that the outlet gas stream was saturated with CO₂ by variation of the flow rate. At 21 °C the nitrogen stream was saturated with 0.21% CO₂, which could be calculated back to a liquid concentration of 0.053 mol/m³. With: $K_2 = K_1/K_W \cdot [CO_2][CO_3^{2-}]/[HCO_3^-]^2$ this leads to $K_2 = 5.8$ (K_2 infinite dilution = 5.8, K_2 ionic effect = 19.6).
- The hydroxyl concentration was measured using a pH-meter. At 21.2 °C a pH of 10.38 was measured. This can be reworked to a hydroxyl concentration of 0.18 mol/m³. Using $K_2 = [CO_3^{2-}]/([HCO_3^-][OH^-])$ this leads to $K_2 = 5.6$. (K_2 infinite dilution = 5.8, K_2 ionic effect = 19.5).

Table 2
Detailed experimental and modelling results

Experimental					Model		
Pressure (bar)	Temperature (°C)	R_A (10 ⁶ mol/s)	J_A^a 10 ³ mol/(m ² s)	$k_L E_A$ 10 ⁵ m/s	$k_L E_A$ 10 ⁵ m/s	Relative diff. %	$\text{OH}_{\text{int}}^-/\text{OH}_{\text{bulk}}^-$ b(-)
0.52	24.0	2.26	0.69	6.19	6.38	3.07	0.79
1.34	24.5	5.34	1.62	5.74	6.04	5.29	0.58
2.02	24.1	7.60	2.31	5.38	5.55	3.12	0.48
3.60	24.0	12.07	3.67	4.80	5.00	4.14	0.34
5.95	24.2	18.04	5.49	4.35	4.50	3.49	0.22
7.54	24.2	22.11	6.73	4.21	4.23	0.55	0.17
10.59	24.2	27.34	8.32	3.70	3.85	3.85	0.12
15.17	23.9	36.07	10.98	3.41	3.43	0.77	0.07

^a $A_{\text{cell}} = 32.9 \text{ cm}^2$.

^b At the end of a penetration time.

The ionic effect on K_2 was therefore not considered in the model. At higher pressures hydroxyl and carbonate ions are severely depleted in the mass transfer zone, which is shown in the last column of Table 2 by the ratio of the concentration of hydroxyl ions at the interface and in the bulk liquid (at the end of a penetration time). A maximum relative deviation of 5% between the model and the experiments was found, which means that the depletions of ions near the interface are described well.

6. Conclusions

The results of this study show that the presented equations and physico-chemical parameters form a consistent set to describe CO₂ absorption in (0.5 M/0.5 M) carbonate/bicarbonate solutions. The Danckwerts criterion as presented in Eq. (2) is justified and could be confined to:

$$m_{\text{CO}_2} c_{\text{CO}_2(\text{G})} \left(\frac{1}{c_{\text{CO}_3^{2-}}} + \frac{2}{c_{\text{HCO}_3^-}} \right) \times \left(\sqrt{1 + \frac{D_{\text{CO}_2} k_{1,\text{app}}}{k_L^2}} - 1 \right) < 0.1$$

to reduce the possible error in the flux calculation to less than 3% when a pseudo-first order reaction is assumed.

Furthermore, experimental validation of the used model was performed in a stirred cell reactor up to CO₂ partial pressures of 16 bar. The criterion becomes more important at these high CO₂ partial pressures, which emphasizes its significance for industrially applied CO₂ removal units operating at elevated pressure.

Notation

A_{cell} geometric surface area of the stirred cell, m²
 c_A concentration of component A, mol m⁻³

D_A diffusion coefficient of component A, m² s⁻¹
 E_A enhancement factor due to the chemical reaction, -
 F Faraday constant, 96485 C mol⁻¹
 $k_{1,\text{app}}$ apparent (pseudo) first order reaction rate constant, s⁻¹
 k_L liquid phase mass transfer coefficient, m s⁻¹
 ℓ_i^∞ ionic conductivity at infinite dilution, m² Ω⁻¹ mol⁻¹
 m ratio of solubility in the liquid phase and in the gas phase, mol m⁻³/(mol m⁻³)
 r_A reaction rate of component A, mol m⁻³ s⁻¹
 R gas constant, 8.314 J mol⁻¹ K⁻¹
 R_A absorption rate of component A, mol s⁻¹
 t time, s
 T temperature, K
 x spatial coordinate, m
 z ionic charge, -

Greek letters

ρ_w density of water, kg m⁻³
 ϕ electrostatic potential gradient, J C⁻¹ m⁻¹
 All other equilibrium and kinetic rate constants are defined in the text.

Subscript and superscript

bulk in the bulk liquid
 int at the interface

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